The nature of the β-peak in the loss modulus of amorphous solids

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Abstract – Glass formers exhibit, upon an oscillatory excitation, a response function whose imaginary and real parts are known as the loss and storage moduli respectively. The loss modulus typically peaks at a frequency known as the α frequency which is associated with the main relaxation mechanism of the super-cooled liquid. In addition, the loss modulus is decorated by a smaller peak, shoulder or wing which is referred to as the β-peak. The physical origin of this secondary peak had been debated for decades, with proposed mechanisms ranging from highly localized relaxations to entirely cooperative ones. Using numerical simulations we bring an end to the debate, exposing a clear and unique cooperative mechanism for the said β-peak which is distinct from that of the α-peak.

Introduction: In Fig. 1 one observes a typical loss modulus, in this case of a film of the metallic glass $Zr_{65}Al_{7.5}Cu_{27.5}$ which was forced at a fixed frequency $\omega = 5440Hz$ while the temperature was changed from 450K to 850K [1]. The main peak represents the typical α relaxation which is the slowest mode of relaxation which is typical to glass formers. When the temperature was at a value such that this relaxation frequency was at resonance with the fixed forcing frequency, the loss of energy registered a maximum. Upon reducing the temperature one sees a wing which becomes obvious at about 650K, this wing is associated with a typical frequency that is higher than the α frequency. This is referred to as a secondary relaxation or the β wing, and in different glassy materials it appears more or less prominent, sometime as a separate peak, and sometime as a shoulder or a wing [2]. Note at this point that the literature is full of other phenomena in glassy relaxation that are referred to as β [3–8]. In this Letter we only deal with the one presented here as in Fig. 1. This is also referred to as the Johari-Goldstein process or the slow β-process [3].

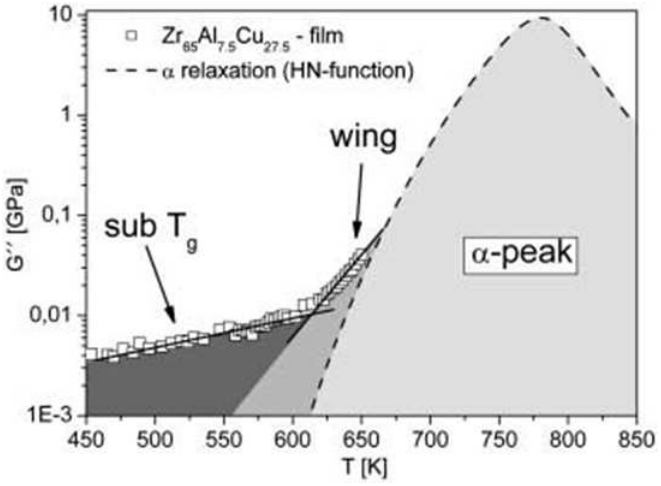

Fig. 1: Color online; a typical loss modulus as a function of temperature. Shown are experimental results for a film of the metallic glass $Zr_{65}Al_{7.5}Cu_{27.5}$ which was forced at a fixed frequency $\omega = 5440Hz$. Note the well defined α peak and the shoulder, or wing, which appears at lower temperatures and is referred to as the β peak. [1].Havriliak-Negami (HN) curve is plotted using parameter $\alpha = 1$ and $\gamma = 0.6$. Please see Ref. [1] for the form of the HN function and other details.

The existence of the β-peak was known for a long time, but its physical origin remained debated. Past explanations can be roughly grouped into two main groups, those involving an extension of the α-relaxation process and those proposing an independent relaxation mechanism. In the first group one can quote for example Dixon et al. [9],

whereas the second group is exemplified by [10]. There seems to be no consensus even on the question whether the β process is local or cooperative. The aim of this Letter is to disperse the fog that had accumulated over the physics of the β-peak and to reach a unique interpretation of the relevant physics. To this aim we use numerical simulations as described next. Of course, numerical simulations are limited in their ability to probe long times, and we are therefore constrained to examine temperatures for which the increase in glassy relaxation times is only 3 to 4 orders of magnitude compared to twelve to fourteen orders in experiments. Nevertheless, we do not expect a fundamental change in physics as the system cools down towards longer and longer relaxation times. This is the basic assumption on which our conclusions rely.

Numerical simulations: As a first step we have reproduced the phenomenology of the β-peak on the machine. To this aim we employed as an example one of the standard models of glass formers, i.e. a binary mixture of point particles interacting via Lennard-Jones potential with three different characteristic interaction lengths $\sigma_{ss} = 1$,$\sigma_{\ell\ell} = 1.4$ and $\sigma_{s\ell} = 1.18$. Details of the potentials can be found for example in Ref. [11]. Of course the phenomenon discussed appears in other models in much the same way, as we have checked by running similar simulations on other models. In the present simulations the unit of length is σ_{ss}, temperature is measured in units such that the Boltzmann's constant equals unity, and time in units of inter-particle distance over the mean velocity. Two dimensional samples, each containing 4900 particles, were firstly quenched slowly (reducing the temperature by 5×10^{-4} in every step) to an inherent state configuration at $T = 0$ using a gradient energy method. We employ periodic boundary conditions keeping the volume of the box fixed. In a second step the samples were raised to a chosen temperature T and were subjected to an oscillatory shear strain $\gamma = \gamma_0 \sin(\omega t)$ according to the affine transformation

$$x_i \to x_i + (\dot{\gamma} dt) y_i, \;\; y_i \to y_i \; . \tag{1}$$

in addition we impose Lees-Edwards boundary conditions. The maximum affine strain is $\gamma_0 = 0.005$, and x_i, y_i are the position of the i'th particle. The Gear predictor-corrector algorithm was used to integrate the sllod equations of motion [12].

The stress in the system was measured using 50 different realizations, and the mean shear stress was fitted to an oscillatory function $\tau_{xy} = \tau_0 \sin(\omega t + \delta)$. The δ corresponds to the phase shift between the strain and the stress. Now, we can calculate the dynamic shear modulus,

$$G = \frac{\tau_0}{\gamma_0} e^{i\delta} \tag{2}$$

where $G = G^{'} + iG^{''}$ is a complex number that depends on the temperature and the shearing frequency. $G^{'}$ and $G^{''}$ are known as the storage and the loss moduli.

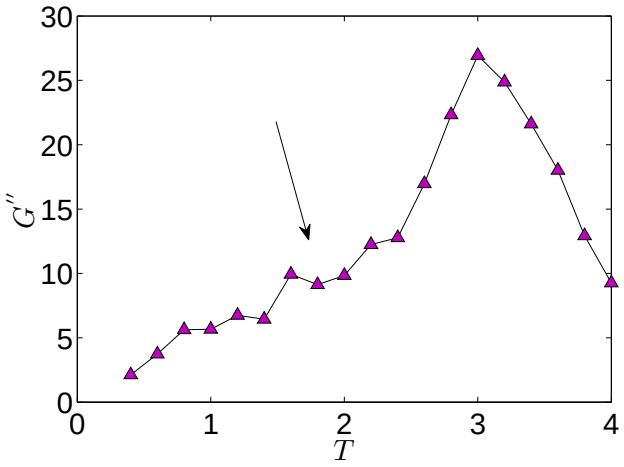

Fig. 2: Color online; the loss modulus $G^{''}$ as a function of temperature from numerical simulations ($\omega = 0.01$). Observe the clearly defined α peak and the distinct β wing.

To produce data which are analogous to the experimental ones in Fig. 1 we studied $G^{''}$ when the system was subject to such a simple oscillatory shear with a fixed frequency Ω for a range of temperatures. A typical result is shown in Fig. 2 which pertains to $\omega = 0.01$ and T in the range $0.5 \leq T \leq 6$. In a satisfactory agreement with the experimental picture we observe a clear α-peak decorated with a distinct β-wing in the range of temperatures $1.0 \leq T \leq 2.0$. Similar simulations done at a fixed temperature with varying frequencies resulted in the same evidence for the existence of the β-process as seen in experiments. We thus feel encouraged to proceed to study the nature of this process.

The β-process, local or cooperative?: presently we can use the power of numerical simulations to answer the first crucial question, is the β-process local or cooperative? To this aim we have selected randomly a small fraction of the particles in our system, and **pinned** them to the coordinate frame that moves with the affine transformation, not allowing them to participate in the relaxation dynamics. We expect that such a procedure should certainly affect the α-peak which is known to be cooperative [13, 14]. As for the β-wing, if it is associated with a local process, a small fraction of pinned particles should not make a big difference. It turns out that a small fraction of pinned particles, say larger than 2.5%, is sufficient to suppress the β-wing altogether. In Fig. 3 we show the results of this exercise with varying percentage of pinned particles, from 0% to 10%. While the α-peak is affected as expected, slightly suppressed and pushed to higher temperatures (the decay process is pushed to lower frequencies) [6], the β-wing is suppressed altogether when the concentration of the pinned particles exceeds 2.5%. We can thus conclude that the β-process must be cooperative rather than local. This immediately excludes the first

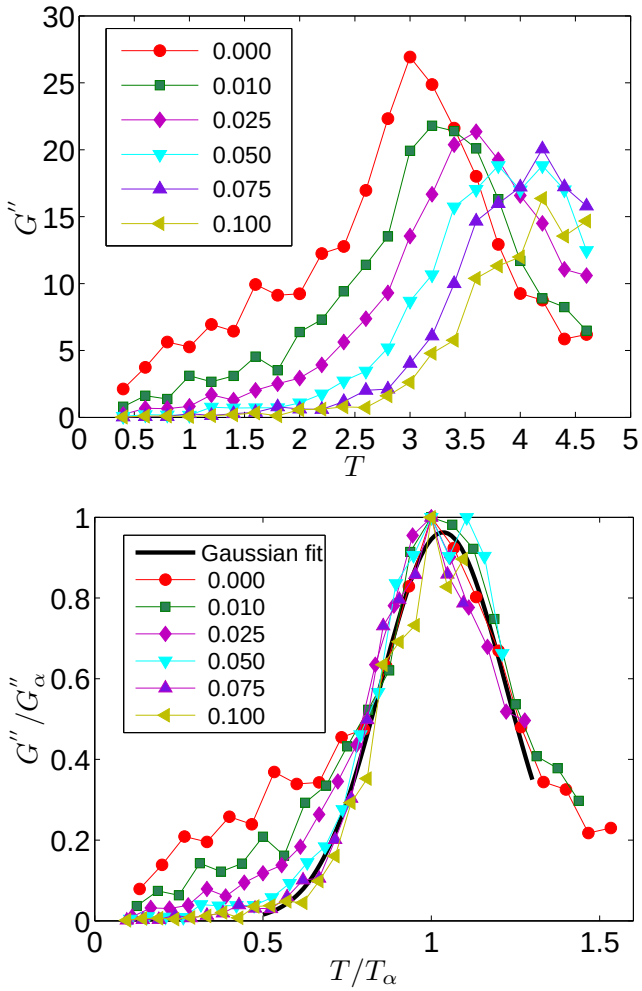

Fig. 3: Color online; Upper panel: the loss modulus as shown in the previous figure, and the loss modulus when a small fraction of particles get pinned. The consequence of varying concentrations of pinned particles are shown. Note that it is sufficient to pin more than 2.5% of the particles to eliminate the β wing altogether. Lower panel: collapse of the data shown in the upper panel, obtained by rescaling the temperature with a characteristic G''_α and T_α, the value and the position of the α peak which depends on the concentration of pinned particles. We see that the β peak is eliminated with all the concentrations larger than 2.5%. The grey curve is a Gaussian fit to the remaining α process.

group of mechanisms discuss above.

Which cooperative mechanism then?: to unfathom the nature of the cooperative β process, we examined carefully the dynamics in our system on time scales of the order of the cage dynamics, i.e. for time scales of the order of unity in our re-scaled units. In Fig. 4 we show the self part of the intermediate scattering function $F_s(q,t)$ for a fixed temperature and various pinning density. $F_s(q,t)$

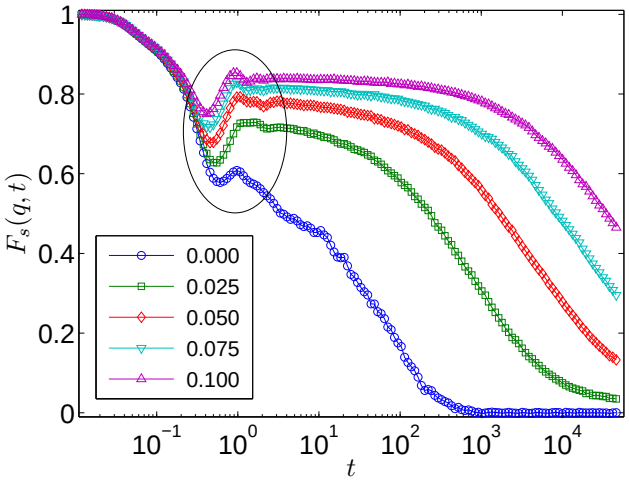

Fig. 4: Color online. The self part of the intermediate scattering function for $T = 3$ for several pinning densities in a 2D system. Note the change of the shape of the function in the encircled area.

is defined as

$$F_s(q,t) = \frac{1}{N'} \left\langle \sum_{j=1}^{N'} e^{\imath \vec{q}\cdot[\vec{r}_j(t) - \vec{r}_j(0)]} \right\rangle, \qquad (3)$$

where N' is the number of particles which are mobile, $\langle \ldots \rangle$ represent thermal average and $\vec{r}_j(t)$ is the position vector of particle j at time t. $\vec{q}$ is chosen uniformly on the surface of a sphere of radius $q = |\vec{q}| = 2\pi/r_0$, where $r_0 = 2^{1/6}$ is the position of the minimum in the potential function as a function of distance. This value roughly corresponds to the first peak position in the static structure factor. We took 128 different directions for the averaging of $F_s(q,t)$. We observe a strong slowing down in the dynamics as we increase the pinning density: the effective τ_α becomes larger. But we also observe a hump in the curve, on time-scales corresponding to the β process, which almost disappear when the concentration of the pinned particles vanishes. This hump can be explained by a recoil motion of a free particle when it collides with a pinned particle. Evidently this phenomenon is less pronounced when the collision occurs with two free particles. In this case, one particle can transfer momentum to its neighbor etc, a process that evolves into a collective motion of number of particles due to the collisions. This cooperative motion is suppressed by the pinned particles.

In left panel of Fig. 5 we show the cumulative displacement of all the particles after four time units (i.e. at $t = 4$ with respect to their position at $t = 0$). We observe long chains of correlated motion of particles all occurring at thermal equilibrium which is maintained only by the influence of random forces. We emphasize that no external forces were applied. The darker arrows are to indicate the particles that move more than 40% of the typical inter-

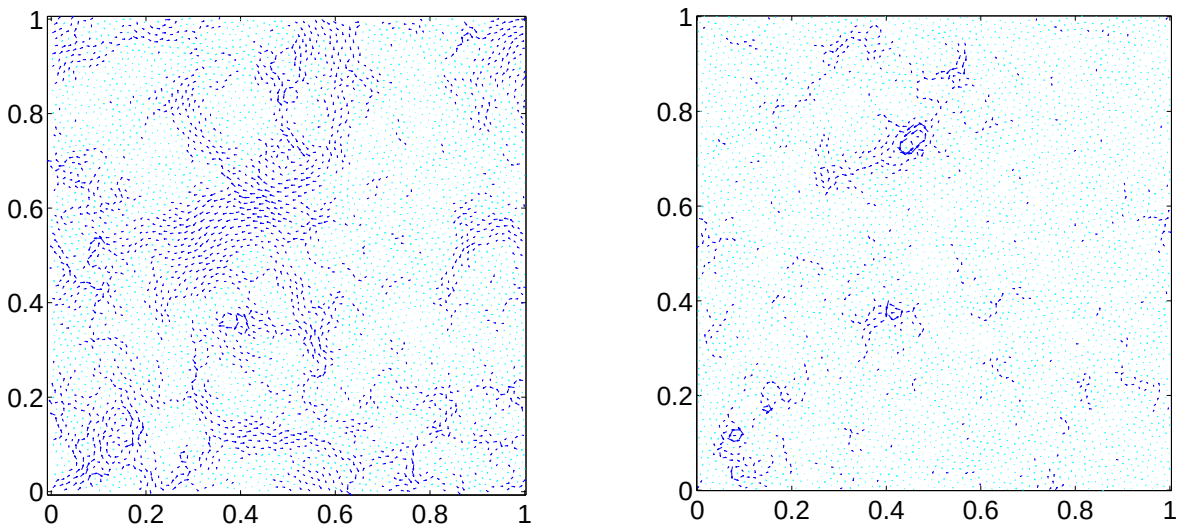

Fig. 5: Color online: Left Panel: a graphic representation of the cooperative motion that is associated with the β wing. Note the chains of particles that have moved coherently during a time span of four time units. The particles that move more than 40% of the typical inter-particle distance are marked in dark blue. Right Panel: similar graphic representation of the suppression of the majority of the cooperative motion that is responsible for the β wing by the addition of 2.5% pinned particles. In contrast to the previous figure, here one needs to look at cumulated motions for 15 time units to see the remnant correlated motion.

particle distance. In comparison, with 2.5% of pinned particles, there is hardly any such correlated motions on the scale of 4 units of time. One has to increase the time window to about 15 units of time, cf. the right panel of Fig. 5, in order to observe the remnant weak cooperative motion.

In summary, we have shown here that the β wing measured in loss moduli has to do with a cooperative motion which is however associated with very fast time scales, of the order of the cage time. The cooperative motion consists of chains of particles that move cooperatively when the system is forced in an oscillatory fashion. Thus cooperative yes, but an extension of the α process no. We trust that the clear cut numerical experiments discussed above should remove any doubt as to the origin of the β wing in the loss modulus.

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